APPENDIX C

Activity and Molar Concentration of Actinides Used in this Investigation

Table C-1. Activity and Molar Concentrations of Actinides Used in this Investigation

Radionuclide	Date	Water	Half-Life (yrs)	Decay constant	Co (CPM/ml)	Molar Conc. (mol/L)
Thorium-230	11.16.98	SPW base	7.540E+04	2.91506E-13	7802	7.40618E-07
		SPW w/o F	7.540E+04	2.91506E-13	8258	7.83905E-07
		SPW w/o CO3	7.540E+04	2.91506E-13	6010	5.70509E-07
		SPW w/o SO4	7.540E+04	2.91506E-13	8182	7.7669E-07
	3.1.99	SPW 0 hr.	7.54E+04	2.91506E-13	20179	1.91553E-06
		SPW 24 hr.	7.54E+04	2.91506E-13	18553.3	1.7612E-06
	8.99	SPW base	7.54E+04	2.91506E-13	41636.9	3.95245E-06
		SPW base	7.54E+04	2.91506E-13	52478	4.98156E-06
		SPW base	7.54E+04	2.91506E-13	1162283	1.10332E-04
Neptunium-237	2.8.99	SPW w/ HA & EDTA	2.140E+06	1.02708E-14	12220	3.29232E-05
		SPW 0 hr.	2.140E+06	1.02708E-14	12153	3.27427E-05
		SPW 24 hr.	2.140E+06	1.02708E-14	12286	3.3101E-05
	4.12.99	SPW w/o F	2.140E+06	1.02708E-14	11966.9	3.22413E-05
		SPW w/o CO3	2.140E+06	1.02708E-14	11935.5	3.21567E-05
		SPW w/o SO4	2.140E+06	1.02708E-14	11987.2	3.2296E-05
	6.99	Exp 11 w/o HA & EDTA	2.140E+06	1.02708E-14	18566	5.00206E-05
		Exp 11 w/ HA & EDTA	2.140E+06	1.02708E-14	18242	4.91477E-05
	7.21.99	SPW w/o CO3 & F	2.140E+06	1.02708E-14	22298.4	6.00765E-05
		SPW w/o CO3 & SO4	2.140E+06	1.02708E-14	20814.5	5.60786E-05
	8.99	SPW base	2.140E+06	1.02708E-14	20729.4	5.58493E-05
		SPW base	2.140E+06	1.02708E-14	20655.6	5.56504E-05
		SPW base	2.140E+06	1.02708E-14	64387.3	1.73473E-04
Americium-241	1.25.99	SPW 0 hr.	4.327E+02	5.07963E-11	4398	2.39585E-09
		SPW 24 hr.	4.327E+02	5.07963E-11	3847	2.09569E-09
	6.99	Exp 11 w/o HA & EDTA	4.327E+02	5.07963E-11	16193	8.82127E-09
Uranium-233	1.25.99	SPW 0 hr.	1.592E+05	1.38063E-13	5322	1.06668E-06
		SPW 24 hr.	1.592E+05	1.38063E-13	5128	1.0278E-06
	3.25.99	SPW w/o F	1.592E+05	1.38063E-13	13143.6	2.63436E-06
		SPW w/o CO3	1.592E+05	1.38063E-13	13242.6	2.6542E-06
		SPW w/o SO4	1.592E+05	1.38063E-13	13826.5	2.77123E-06
		SPW w/o CO3,SO4	1.592E+05	1.38063E-13	30742.9	6.16176E-06
		SPW w/o CO3,F	1.592E+05	1.38063E-13	29066.7	5.8258E-06
		DDI pH 7.6-8.5 (column 1)	1.592E+05	1.38063E-13	14588	2.92386E-06
		DDI pH 7.6-8.5 (column 3)	1.592E+05	1.38063E-13	14588	2.92386E-06
Plutonium-239	3.1.99	SPW 0 hr - Pu(IV)	2.410E+04	9.12015E-13	9375.8	2.84474E-07
		SPW 24 hr - Pu(IV)	2.410E+04	9.12015E-13	8565.9	2.599E-07

APPENDIX D

Colloid Attenuation by Interbed Columns

Colloid Attenuation by Interbed Columns

A series of column experiments was conducted to determine (1) the efficacy of washing columns to remove colloidal fines from the column packing material and (2) to determine if either associated or true colloids were attenuated in the columns by the interbed composite soil. To conduct these experiments, the composite interbed soil was sieved to isolate the 106-250 μm particle fraction. Replicate columns were packed with this particle size fraction using the packing techniques discussed in Chapter 3.

The first experiment was designed to determine if colloids were washed from the column during the first few pore volumes of eluant. A spiking solution containing approximately 0.18 μCi of ^{238}Pu was added to 15.7 ml of the PWS followed by pH adjustment to ≈9.2. Approximately one pore volume of the spiking solution was introduced into each of the replicate columns and eluted for approximately 200 pore volumes. The particulate fraction in the column effluent was determined by filtering selected eluant fractions using 0.02-μm x 25-mm syringe filters.

A second experiment was conducted using the replicate columns from the first experiment and represented packed columns that had been washed for 200 pore volumes. A Pu spiking solution was prepared similar to the above preparation and spiked onto the columns as noted above. Again, eluant fractions were filtered to determine the particulate fraction.

A third experiment using the same packed columns, representing packed columns washed with 400 pore volumes of the PWS, was conducted to determine the degree to which associated colloids were attenuated by the column packing. A suspension of interbed colloids <0.2 μm was prepared by mixing interbed particles <106 μm in the PWS by shaking for 24 hours, and filtering at 0.45 μm and then at 0.2 μm . Approximately 0.18 μCi of ^{238}Pu was added to the colloidal suspension and shaken for 24 hours to tag the interbed colloids. A one-pore volume spike of the colloidal suspension was introduced into the pair of columns and eluted for 200 pore volumes with the PWS. As noted above, eluant fractions were filtered at 0.2 μm to determine the particulate fraction in the column effluents.

Results of these experiments are summarized in Table D-1. Results from the first set of experiments show breakthrough from columns 1 and 2 to be 29 and 27 % respectively and the particulate fraction between 83 and 90 %. Filtration of the original spiking solution after 24 hours indicated that 40 to 47 % was in particulate form, likely plutonium oxy-hydroxide colloids. The remainder of the particulate fraction (83-90 % less 40-47 %) may have been colloidal "fines" from the unwashed column. If this was true, results from the second set of experiments should indicate a particulate fraction near 50 % if in fact colloidal "fines" were efficiently washed from the columns during the 200-pore volume eluant. Results from the second pair of columns show breakthrough of 34 % with a particulate fraction between 54 and 72 %, consistent with expectations. In the third set of columns, colloids (<0.2 μm) were introduced into the washed columns and one would expect a significant portion of the

colloidal mass to be retained in the column. In experiment 3, breakthrough was in fact reduced from approximately 30 % to 12 and 17% respectively, and the particulate fraction was reduced. This suggests that the columns effectively attenuated colloids from the spiking solution.

In summary, the data from experiments 1 and 2 suggest that the column matrix can attenuate true colloids and the data from experiment 3 that the column matrix also attenuates associated colloids (from experiment 3). Recalling that the columns were packed with interbed particles within a range of 106 to 250 μm, columns packed with interbed soil < 250 μm to include particles <106 μm should more effectively attenuate both true and associated colloids.

Table D-1. Results of Colloid Attenuation Experiments

Experiment-Column	Breakthrough -%	Particulate Pu-%
Expt 1, Col 1	29	85-90
Expt 1, Col 2	27	83-90
Expt 2, Col 1	34	65-72
Expt 2, Col 2	34	54-72
Expt 3, Col 1	12	11-23
Expt 3, Col 2	17	10-17

APPENDIX E

Plutonium Oxidation State Analysis Procedure

Plutonium Oxidation State Analysis

The Bis(2-ethylhexyl) hydrogen phosphate (HDEHP) extraction was used to determine the oxidation state of plutonium in the absence of a holding oxidant. It was also performed on americium, neptunium, and uranium samples to verify the procedure.

HDEHP Extraction (Neu, *et al.*, 1994)

This process involves four separate extractions, which when combined yielded an oxidation state distribution for an aqueous sample of plutonium solution. The four extractions are as follows:

1. Extraction of Pu (IV) into organic phase
2. Extraction of Pu (III) and Pu (IV) into organic phase
3. Extraction of Pu (IV) and Pu (VI) into organic phase
4. Extraction of Pu (III), Pu (IV), Pu (V), and Pu (VI) into organic phase. The Pu remaining in the aqueous phase is termed "unextractable" and is assumed to be in the Pu (IV) polymeric form or in an unextractable complex.

Required Chemicals

I. 2.25 mL of plutonium solution
II. 99% thenoyltrifluoroacetone (TTA)
III. 99% toluene
IV. 1.0 M HCl
V. 5.0 M HCl
VI. 99% HDEHP
VII. 99% $K_2Cr_2O_7$
VIII. Wallac/LKB 'HiSafe'2 liquid scintillation cocktail

Required Equipment

- 2 Calibrated adjustable 100-1000 µl Eppendorf pipettor and tips (at 0.25 and 0.50 mL)
- twelve 2-dram vials
- Centrifuge for the 2-dram vials
- Timer
- 20 mL plastic liquid scintillation vials with poly-seal caps (9 per analysis)
- Wallac liquid scintillation detector

Initial Steps

1. Dissolve 2.22 g of the 99% TTA in 20 mL of toluene in a glass scintillation vial that has been covered in aluminum foil to prevent exposure of the solution to light. This will yield a solution that is 0.5 M TTA. This solution will photo-decompose, turning from pale yellow to copper, so it should be stored in a drawer away from light and made just prior to use to minimize the effects of this decomposition.
2. Transfer 3.225 g (3.3 mL) of HDEHP solution into 20 mL of toluene to yield a solution that is 0.5 M in HDEHP.
3. Add 0.02354 g of $K_2Cr_2O_7$ to 20 mL of 1 .0 M HCl solution to yield a solution that is 1.0 M in HCl and 4.0 m.M in $K_2Cr_2O_7$ [8.0 mM in Cr (VI)].
4. Prepare nine 20 mL plastic liquid scintillation vials by filling each with 10 mL of 'HiSafe'2. These should be placed in two separate protocols due to the difference in quench for the solutions. One protocol should be used for the two TTA/organic samples and another for the aqueous and HDEHP/organic samples.

Extraction Procedure

1. Transfer a 0.25 mL aliquot of the plutonium solution to one of the scintillation vials filled with 'HiSafe'2 to determine the Pu concentration in the original sample.

Extraction 1 - determination of Pu (IV)

2. Transfer 0.5 mL of the TTA/toluene solution to one of the 2-dram vials.
3. Add 0.5 mL of 1.0 M HCl solution to this 2-dram vial.
4. To a second 2-dram vial, add 0.10 mL of 5.0 M HCl solution.
5. Add 0.5 mL of the plutonium solution to the vial containing the 5.0 M HCl and gently swirl to ensure complete mixing.

6. Pour the contents of the vial containing the TTA solution into the vial containing the Pu solution. Be sure to completely empty both the aqueous and organic phases from the vial.

   Cap the vial and shake gently for 2m 30s to ensure complete extraction.
7. Centrifuge the vial to facilitate phase separation. Be sure to carefully counterbalance the centrifuge.
8. Place 0.25 mL of the organic phase [Pu (IV)] into one of the scintillation vials filled with 'HiSafe'2.
9. Transfer 0.5 mL of the aqueous phase into a clean 2-dram vial. Depress the pipettor as the tip travels through the organic phase, using the air stream to prevent the introduction of any organic phase into the sample. Now transfer 0.25 mL of this aqueous solution [Pu (III), Pu (V), Pu (VI), and Pu (P)] into one of the scintillation vials filled with 'HiSafe'2, again taking caution to avoid drawing any of the thin film of organic phase from the top of the sample.

Extraction 2 - determination of Pu (III + IV)

Note that extraction 2 is identical to extraction 1, with the exception substituting a 1.0 M HCL/4.0 mM $K_2Cr_2O_7$ solution for the 1.0 M HCl solution from step 2 in step 11. This serves to oxidize any Pu (III) to Pu (IV), which will subsequently be extracted into the TTA/organic phase.

10. Transfer 0.5 mL of the TTA/toluene solution to one of the 2-dram vials.

11. Add 0.5 mL of 1.0 M HC/4mM $K_2Cr_2O_7$ solution to this 2-dram vial.

12. To a second 2-dram vial, add 0. 10 mL of 5.0 M HCl solution.

13. Add 0.5 mL of the plutonium solution to the vial containing the 5.0 M HCl and gently swirl to ensure complete mixing.
14. Pour the contents of the vial containing the TTA solution into the vial containing the Pu solution. Be sure to completely empty both the aqueous and organic phases from the vial.

    Cap the vial and shake gently for 2m 30s to ensure complete extraction.

15. Centrifuge the vial to facilitate phase separation. Be sure to carefully counterbalance the centrifuge.
16. Place 0.25 mL of the organic phase [Pu (III), Pu (IV)] into one of the scintillation vials filled with 'HiSafe'2.
17. Transfer 0.5 mL of the aqueous phase into a clean 2-dram vial. Depress the pipettor as the tip travels through the organic phase, using the air stream to prevent the introduction of any organic phase into the sample. Now transfer 0.25 mL of this aqueous solution [Pu (V), Pu (VI), and Pu (P)] into one of the scintillation vials filled with 'HiSafe'2, again taking caution to avoid drawing any of the thin film of organic phase from the top of the sample.

Extraction 3 - determination of Pu (IV + VI)

Note that extraction 3 is identical to extraction 1 except for the substitution of a 0.5 M HDEHP/toluene solution for the TTA/toluene solution from step 1 in step 18. The HDEHP will extract both Pu (IV) and Pu (VI) from the aqueous solution.

18. Transfer 0.5 mL of the HDEHP/toluene solution to one of the 2-dram vials.

19. Add 0.5 mL of 1.0 M HCl solution to this 2-dram vial.

20. To a second 2-dram vial, add 0.10 mL of 5.0 M HCl solution.

21. Add 0.5 mL of the plutonium solution to the vial containing the 5.0 M HCl and gently swirl to ensure complete mixing.
22. Pour the contents of the vial containing the HDEHP solution into the vial containing the Pu solution. Be sure to completely empty both the aqueous and organic phases from the vial.
    Cap the vial and shake gently for 2m 30s to ensure complete extraction.
23. Centrifuge the vial to facilitate phase separation. Be sure to carefully counterbalance the centrifuge.
24. Place 0.25 mL of the organic phase [Pu (IV), Pu (VI)] into one of the scintillation vials filled with 'HiSafe'2.
25. Transfer 0.5 mL of the aqueous phase into a clean 2-dram vial. Depress the pipettor as the tip travels through the organic phase, using the air stream to prevent the

introduction of any organic phase into the sample. Now transfer 0.25 mL of this aqueous solution [Pu (III), Pu (V), Pu (P)] into one of the scintillation vials filled with 'HiSafe'2, again taking caution to avoid drawing any of the thin film of organic phase from the top of the sample.

Extraction 4 - determination of Pu (III + IV + V + VI)

Note the extraction 4 is identical to extraction 2 except for the substitution of HDEHP/toluene solution for the TTA/toluene solution from step 10 in step 26. In this extraction, the dichromate solution oxidizes the Pu (III) to Pu (IV) and the Pu (V) to Pu (VI), both of which are subsequently extracted by the HDEHP.

26. Transfer 0.5 mL of the HDEHP/toluene solution to one of the 2-dram vials..
27. Add 0.5 mL of 1.0 M HCl/4.0 mM $K_2Cr_2O_7$ solution to this 2-dram vial.
28. To a second 2-dram vial, add 0.10 mL of 5.0 M HCl solution.
29. Add 0.5 mL of the plutonium solution to the vial containing, the 5.0 M HC1 and gently swirl to ensure complete mixing.
30. Pour the contents of the vial containing the HDEHP solution into the vial containing the Pu solution. Be sure to completely empty both the aqueous and organic phases from the vial.
    Cap the vial and shake gently for 2m 30s to ensure complete extraction.
31. Centrifuge the vial to facilitate phase separation. Be sure to carefully counterbalance the centrifuge.
32. Place 0.25 mL of the organic phase [Pu (III), Pu (IV), Pu (V), Pu (VI)] into one of the scintillation vials filled with 'HiSafe'2.
33. Transfer 0.5 mL of the aqueous phase into a clean 2-dram vial. Depress the pipettor as the tip travels through the organic phase, using the air stream to prevent the introduction of any organic phase into the sample. Now transfer 0.25 mL of this aqueous solution [Pu (P)] into one of the scintillation vials filled with 'HiSafe'2, again taking caution to avoid drawing any of the thin film of organic phase from the top of the sample.

34. Count each sample for 10 minutes using the Wallac liquid scintillation detector. Determination of the oxidation state distribution may be obtained via a mass balance on plutonium during each extraction step of the process.

The mass balance algorithm shown in Table E-1 was used to determine the plutonium fraction in each oxidation state for the extraction.

Table E-1. Oxidation state determination algorithm for the HDEHP extraction procedure

Oxidation States	Phase	Counts, DPM 0.25 mL	Volume per Extraction (mL)	Fraction in Oxidation State	Fraction Recovered
ALL	Original Sample	C_o	0.5	-	
IV	TTA Organic	C_1	0.5	$\frac{0.5\,C_1}{0.5C_1+1.1C_2}$	$0.5C_1+1.1C_2$ $0.5C_o$
III, V, VI, P	TTA Aqueous	C_2	1.1	$\frac{1.1C_2}{0.5C_1+1.1C_2}$	$0.5C_1+1.1C_2$ $0.5C_o$
III, IV	TTA/Cr Organic	C_3	0.5	$\frac{0.5\,C_3}{0.5C_3+1.1C_4}$	$0.5C_3+1.1C_4$ $0.5C_o$
V, VI, P	TTA/Cr Aqueous	C_4	1.1	$\frac{1.1C_4}{0.5C_3+1.1C_4}$	$0.5C_3+1.1C_4$ $0.5C_o$
IV, VI	HDEHP Organic	C_5	0.5	$\frac{0.5\,C_5}{0.5C_5+1.1C_6}$	$0.5C_5+1.1C_6$ $0.5C_o$
III, V, P	HDEHP Aqueous	C_6	1.1	$\frac{1.1C_6}{0.5C_5+1.1C_6}$	$0.5C_5+1.1C_6$ $0.5C_o$
III, IV, V, VI	HDEHP/Cr Organic	C_7	0.5	$\frac{0.5\,C_7}{0.5C_7+1.1C_8}$	$0.5C_7+1.1C_8$ $0.5C_o$
P	HDEHP/Cr Aqueous	C_8	1.1	$\frac{1.1C_8}{0.5C_7+1.1C_8}$	$0.5C_7 1.1C_8$ $0.5\,C_o$

APPENDIX F

Aging Filtration Experimental Data

Table F-1. Summary of aging filtration experiments

		Time	Unfiltered 1 (cpm)	Unfiltered 2 (cpm)	Average (cpm)	Filtered 1 (cpm)	Filtered 2 (cpm)	Average (cpm)	Soluble fraction	RPD
Americium	pH 2	0	4597	4490	4543	4584	4575	4580	100.8	0.023
		4	4539	4518	4528	4558	4550	4554	100.6	0.005
		12	4640	4613	4627	4673	4675	4674	101.0	0.006
		24	4675	4717	4696	4690	4704	4697	100.0	0.009
	PH 8	0	3771	3728	3749	739	723	731	19.5	0.011
		4	2938	2866	2902	500	498	499	13.3	0.025
		12	2731	2720	2726	146	148	147	3.9	0.004
		24	2694	2564	2629	33	22	28	0.7	0.049
Uranium	pH 2	0	5325	5204	5264	5271	5253	5262	100.0	0.023
		4	5286	5264	5275	5265	5264	5265	99.8	0.004
		12	5257	5298	5277	5276	5305	5290	100.2	0.008
		24	5345	5299	5322	5348	5352	5350	100.5	0.009
	PH 8	0	5250	5211	5230	5140	5102	5121	97.9	0.007
		4	5216	5210	5213	5168	5081	5124	98.3	0.001
		12	5203	5204	5204	5230	5124	5177	99.5	0.000
		24	5340	5309	5324	5191	5157	5174	97.2	0.006

Table F- 1 (continued). Summary of aging filtration experiments

		Time	Unfiltered 1 (cpm)	Unfiltered 2 (cpm)	Average (cpm)	Filtered 1 (cpm)	Filtered 2 (cpm)	Average (cpm)	Soluble fraction	RPD
Neptuniurn	pH 2	0	3773	3763	3768	3812	3767	3789	100.6	0.003
		4	3840	3790	3815	3811	3828	3820	100.1	0.013
		12	3826	3832	3829	3856	3815	3836	100.2	0.002
		24	3867	3903	3885	3877	3893	3885	100.0	0.009
	pH 8	0	4186	4110	4148	4120	4039	4079	98.4	0.018
		4	4118	4120	4119	3948	3959	3953	96.0	0.000
		12	4158	4193	4175	4002	3920	3961	94.9	0.009
		24	4256	4230	4243	3989	3945	3967	93.5	0.006
Thorium	pH 2	0	1518	1478	1498	1472	1460	1466	97.9	0.026
		4	1522	1525	1524	1426	1445	1436	94.2	0.002
		12	1521	1516	1519	1451	1434	1443	95.0	0.004
		24	1560	1554	1557	1517	1476	1496	96.1	0.004
	pH 8	0	8128	7964	8046	66	68	67	0.8	0.020
		4	6968	6945	6957	61	69	65	0.8	0.003
		12	6745	6528	6636	66	61	63	0.8	0.033
		24	5468	6048	5758	59	59	59	0.7	0.101

Table F- 1 (continued). Summary of aging filtration experiments

		Time	Unfiltered 1 (cpm)	Unfiltered 2 (cpm)	Average (cpm)	Filtered 1 (cpm)	Filtered 2 (cpm)	Average (Ccpm)	Soluble fraction	RPD
Plutonium(IV)	pH 2	0	3886	3884	3885	3673	3638	3655	94.1	0.000
		4	3923	3959	3941	3653	3698	3675	93.3	0.009
		12	3953	4004	3978	3737	3651	3694	92.9	0.013
		24	4035	4026	4031	1722	3710	3716	92.2	0.002
	pH 8	0	3755	3742	3749	2199	1784	1991	53.1	0.003
		4	3830	3829	3830	1414	1840	1627	42.5	0.000
		12	3873	3857	3865	1597	1566	1581	40.9	0.004